CHAPTER VI: SUMMARY

Zinc oxide (ZnO) is highly important material which possesses many unique optical and electrical properties for applications in many important industry areas, such as solar cells, electrodes, gas sensors, catalysts and so on. With the development of research on fabrication and applications of ZnO particles and films, more and more valuable research results have verified that the morphology of ZnO particles and films plays the key role for the applications of ZnO in special fields. So far, a wide variety of ZnO special morphologies, complex structures and films have been fabricated using physical or chemical methods. However, the work on the controlled growth of ZnO intentionally is still in developing state. Therefore the methods for tailoring the morphology of ZnO particles and films according to the will of human are quite demanded.

The development of low-cost, colorful dye sensitized solar cells is an imperative for producing environmentally clean alternative energy resources (green energy). Commonly, nanocrystalline TiO_2 has been used as a photo- material in DSSCs since the first demonstration by Gratzel and his co-workers. Other n-type metal oxide semiconductors, such as ZnO, SnO_2, In_2O_3 and Nb_2O_5 etc, can also be used in DSSCs from a principle point of view. Among all, ZnO is a versatile, wide-bandgap semiconductor and has recently been reported as an alternative for DSSCs because bulk ZnO offers a large band gap of 3.37 eV, which is comparable to TiO_2 and has very high electron mobility, which is about 155 $cm^2\ V^{-1}\ s^{-1}$ for high quality thin film. This is primarily due to the high mobility of conduction electrons in the material and good chemical and thermal stability under operating conditions. The DSSC is surface related phenomenon and ZnO possess various nanostructures provides large surface area for dye adsorption, thus can be effectively used for dye sensitized solar cell application.

In the present work, nanostructured ZnO thin films have been deposited by, relatively economical, and simple methods i.e. chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR). The synthesis of ZnO films were carried out by only CBD, only SILAR or by combination of both using different precursor solutions at different conditions depicted in chart below. These methods are used to deposit nanocrystalline thin films. The preparative parameters of each method have been optimized to achieve nanocrystalline and porous films so that they give higher surface area for dye adsorption which is basic need for dye sensitized solar cell.

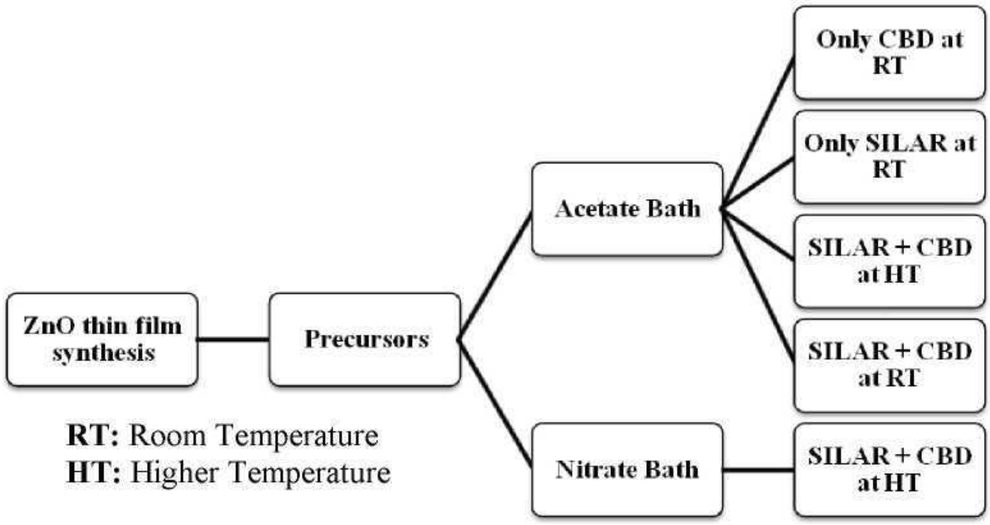


Chart 6.1 Schematic representations depicting the synthesis of ZnO film via different route with different precursors

Following summarized the different chapters

- **Chapter 1:** Introduction

  A brief introduction and background to the ZnO and synthesis of ZnO films using different methods as well as its application in dye sensitized solar cell was given. The aims of the research were highlighted.

- **Chapter 2:** Theoretical background

  The theoretical background of deposition methods for ZnO film, details about chemical bath deposition (CBD) method, successive ionic layer adsorption and reaction (SILAR) technique and characterization techniques were introduced. Also theoretical background of DSSC was included in details.

- **Chapter 3:** Synthesis and characterization of ZnO thin films

  In this chapter, the focus was made to synthesize ZnO film with different morphologies in order to utilize for DSSC. Different characterizations were performed and results were discussed by keeping in mind, the use of this ZnO for DSSC application.

- **Chapter 4:** Device grade development of DSSC by using chemically grown ZnO

  Initial part of this chapter was focused on the construction of device grade DSSC with the structure

  FTO/nanoporous ZnO/dye/electrolyte/back contact

  Next part was focused on the optimization of different parameters as: the seeded ZnO, nanoporous ZnO, dye and electrolyte towards efficient device. In this, initially all parameters were optimized by using Eosin-Y as a sensitizer. The final structure for efficient DSSC was

FTO/seeded or compact ZnO/nanoporous ZnO/dye/electrolyte/back contact

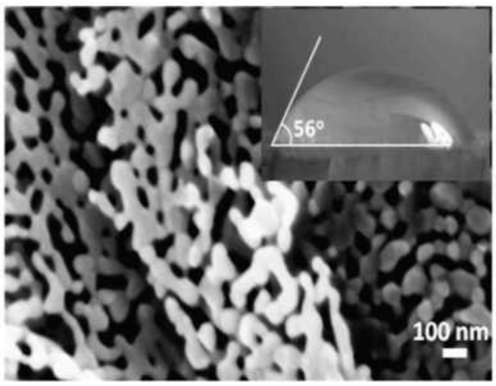
- **Chapter 5:** Efforts towards higher efficiency and advance colorful approach

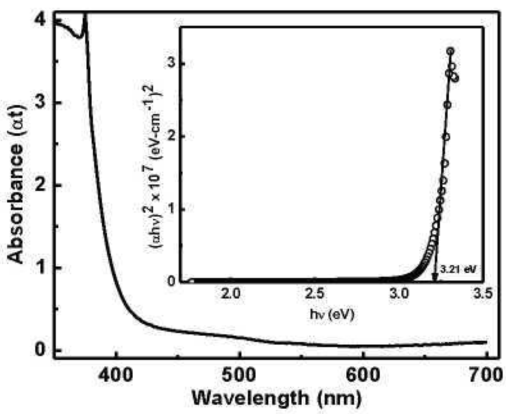
  In this, efforts were made toward higher efficiency for chemically synthesized ZnO film. Different dyes with different absorption spectra were used and checked for device performance. This opens the way for colorful DSSC. Also, advance colorful approach was discussed by mixing three different basic color dyes and their effect on the device performance.

- **Chapter 6:** Summary

  From all the studies it is concluded that various nanostructures of ZnO film synthesized by CBD and SILAR shows good photovoltaic response towards DSSCs. For each method, the nanostructure can be tuned by optimizing preparative parameters. Among various nanostructures, the 'sand rose' like morphology of ZnO nanoporous film synthesized by CBD over seeded ZnO exhibited the highest efficiency (η = 1.69 % for Eosin-Y dye). The enhancement of efficiency was observed for dye parameters optimization followed by optimization of liquid electrolyte with optimized ZnO film.

Preparative parameters	Optimized conditions
Deposition time for CBD	20 hours
Deposition temperature for CBD	27 °C
Zinc acetate concentration for CBD	0.2 M/L
Annealing temperature	200 °C
Annealing time	1 hour
Number of SILAR cycles	25
Zinc acetate concentration for SILAR	0.1 M/L
Dye concentration	300 μM/L
Dye soaking time	15 min
Dye soaking temperature	80 °C
Iodine concentration	0.1 M/L
Ethylene carbonate:Acetonitrile (AC:EC)	20:80 volume ratio





The highest efficiency achieved for optimized Eosin-Y dye and electrolyte with sand rose like ZnO structure was 2.16 %.

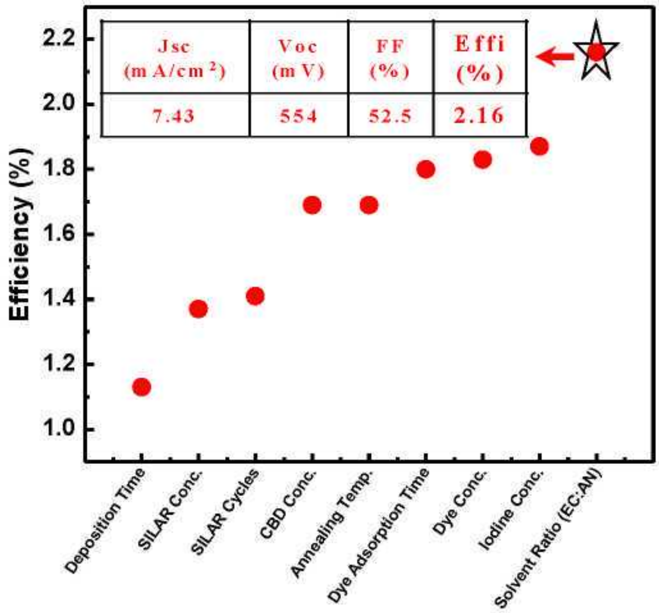


Figure 6.1 Step wise improvement in efficiency as a function of different parameters. Inset shows the values for PV parameters of final optimized device with EY dye as sensitizer.

Furthermore utilizing the optimized structure of ZnO and other parameters for which it shows highest efficiency with ZnO was used to fabricate colorful DSSCs with different metal free dyes namely, Rose Bengal, Rhodamine B, Coumarin 343, Methylene Blue, and Mercurochrome, etc. including Eosin-Y and there performance were checked and listed in table 6.1. The limit to the efficiency for metal free dyes is limited spectral coverage in visible region of solar spectrum. Hence, in order to achieved higher efficiency the used of metal free D149 dye from indoline series and Ru-metal based N719 dye having wide spectral coverage in visible region, which is responsible for producing higher current and ultimately enhance the efficiency of device (η=3.43 % and 3.09 %, respectively). Moreover, efforts have been made towards advance colorful approach on optimized structure with combination of two basic color dyes in order to cover whole region of visible spectra. For example the mixing of Eosin-Y (red) with Coumarin 343 (yellow) results in orange color which covers maximum part of visible spectra than individual dye which is responsible for enhancement in efficiency (2.25 %) than individual one.

Thus the final conclusion is that though the fibrous ZnO nanoflakes and nanoparticles ZnO films deposited at room temperature using cost effective CBD method and SILAR technique, the DSSC performance of these films was quite good with inexpensive dyes, makes them promising for commercial production of low-cost and colorful device grade DSSCs.

Table 6.1 Photovoltaic properties of DSSCs based on soft chemically grown ZnO film with different dyes

	Photoanode	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	J_o (mA/cm^2)	R_S (kΩ)	R_{SH} (kΩ)	η (%)
ZnO		0.000118	376	77	0.008	4122	394	0.03
N3		1.29	428	62.9	0.011	45.4	∞	0.34
EY		7.43	554	52.5	0.022	34.3	2521	2.16
Rhod B		4.61	449	61.15	0.0068	22.7	6405	1.26
Rose B		5.04	458	54.93	0.0164	34.3	18838	1.27
C343		4.07	476	60.0	0.033	28.6	588	1.16
MC		6.42	526	55.2	0.0113	24.6	3217	1.86
MB		0.22	224	45.78	0.0125	352.5	3012	0.02
EY+C343		7.49	528	56.9	0.023	22.5	1399	2.25
D149		15.05	514	44.3	0.065	22.8	910	3.44
N719		11.21	530	52	0.018	16.97	1349	3.09